Excitation-Wavelength Dependent and Time-Resolved Photoluminescence Studies of Europium Doped GaN Grown by Interrupted Growth Epitaxy (IGE)

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ABSTRACT

The emission properties of Eu doped GaN thin films prepared by interrupted growth epitaxy (IGE) were investigated through excitation-wavelength dependent and time-resolved photoluminescence (PL) studies. Under above-gap excitation (333-363 nm) large differences were observed in the Eu^{3+} PL intensity and spectral features as a function of Ga shutter cycling time. The overall strongest red Eu^{3+} PL intensity was obtained from a sample grown with a Ga-shutter cycling time of 20 minutes. The main Eu^{3+} emission line originating from $^5D_0 \rightarrow {}^7F_2$ transition was composed of two peaks located at 620 nm and 622 nm, which varied in relative intensity depending on the growth conditions. The room-temperature emission lifetimes of the samples were non-exponential and varied from ~50 μs to ~200 μs (1/e lifetimes). Under resonant excitation at 471 nm ($^7F_0$->$^5D_2$) all samples exhibited nearly identical PL spectra independent of Ga shutter cycling time. Moreover, the Eu^{3+} PL intensities and lifetimes varied significantly less compared to above-gap excitation. The excitation wavelengths dependent PL results indicate the existence of different Eu^{3+} centers in GaN: Eu, which can be controlled by the Ga shutter cycling time.

INTRODUCTION

Rare-earth (RE) doped III-V compound semiconductors have received significant attention due to their applications in light emitting devices and for their unique optical and electrical characteristics [1,2]. In recent years, RE ions have been introduced into GaN for optoelectronic devices operating in the ultraviolet (UV), visible, and infrared (IR) spectral region [1,2]. Eu^{3+} doping of GaN has been of particular interest because of its efficient red emission at ~ 622 nm used in electroluminescence (EL) devices [2]. In addition, Eu^{3+} exhibits a relatively simple energy diagram, which makes Eu^{3+} an excellent spectroscopic probe [3-5]. The ground state level $^7F_0$ and the lowest emitting level $^5D_0$ of Eu^{3+} are non-degenerate. Therefore, the optical transition $^5D_0 \rightarrow {}^7F_0$ can provide important information on different Eu^{3+} centers in the GaN lattice.

The main aim of this research is to develop compact, efficient, and bright EL devices based on RE doped GaN thin films. To achieve this goal, the materials need to be optimized for several growth parameters: e.g. RE concentration, growth temperature, and III/V ratio. In this work, a set of GaN:Eu samples was prepared by a new growth technique called “Interrupted Growth Epitaxy” (IGE) [6]. During IGE the group III (Ga) shutter is closed for a certain time interval, which allows the GaN: Eu film to compensate for any nitrogen deficiency. Improvements in the GaN: Eu EL device performance by more then an order of magnitude were

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observed from GaN: Eu films grown by IGE compared to conventional MBE [6]. Initial studies of the photoluminescence (PL) properties of these samples are presented in this paper.

EXPERIMENTAL PROCEDURES

IGE was recently developed at the University of Cincinnati in order to determine the optimum group V/III growth ratio for GaN: Eu. Closing the Ga shutter for a certain time interval allows the GaN:Eu film to compensate for any nitrogen deficiency. A set of Eu doped GaN films with group III (Ga) shutter open times of 5, 10, 15, 20, 30, and 60 min were grown using IGE technique on Si substrates. A full growth run of Eu doped GaN covered a time period of 60 minutes. For the main growth, the substrate temperature was ramped to 650 °C and the Ga cell temperature was 900 °C. The Eu cell temperature was 440 °C, resulting in an estimated Eu concentration of ~0.1 at. % [6].

PL measurements were performed using the UV argon laser line (333.6-363.8) nm for above-gap excitation. Resonant pumping into the $^7F_0 \rightarrow {}^5D_2$ Eu^{3+} transition at ~ 471 nm was obtained using the output of a Nd:YAG pumped Optical Parametric Oscillator (OPO) system. For temperature-dependent PL measurements, the sample temperature was controlled between 15 K and 300 K using a two-stage closed-cycle helium refrigerator. The visible luminescence was analyzed by a 0.5 or 1-m monochromator and detected with a thermo-electric cooled photomultiplier tube (PMT). PL lifetime data were taken with the third harmonic output of a pulsed Nd:YAG laser (355-nm) for above-gap excitation and the OPO system operating at ~ 471 nm for resonant excitation. The luminescence signal was processed using either a lock-in amplifier or a boxcar averager and PL decay curves were recorded using a digitizing oscilloscope.

RESULTS AND DISCUSSION

Above-gap emission spectra and PL decay

Figure 1 shows an overview of the room-temperature PL spectra of Eu doped GaN for various Ga shutter cycling times. The PL was excited using an UV argon laser (333.6-363.8 nm), which corresponds to above-gap pumping. The characteristic Eu^{3+} red emission at ~ 622 nm attributed to the intra-4f $^5D_0 \rightarrow {}^7F_2$ transition was observed in all samples accompanied by other Eu^{3+} lines at ~ 601 nm ($^5D_0 \rightarrow {}^7F_1$) and ~ 663 nm ($^5D_0 \rightarrow {}^7F_3$). The strongest red emission was observed from GaN:Eu with a shutter cycling time of 20 min as illustrated in Fig. 1 (a). The integrated PL intensity as a function of Ga shutter cycling time is also depicted in Fig. 1 (b).

It can be noticed from Fig. 1, that the main red emission line consisted of two peaks at ~ 620 nm and ~ 622 nm. The intensity ratio of these two PL lines changed as a function of Ga shutter cycling time. The GaN:Eu sample with the strongest Eu^{3+} PL intensity exhibited mainly emission from the 620 nm PL line. The observation of two strong $^5D_0 \rightarrow {}^7F_2$ PL lines suggests the existence of two dominant Eu^{3+} sites (labeled in the following as site 1 and site 2). It is also interesting to note that the PL line at ~ 633 nm was unusually pronounced in some GaN:Eu samples, and was correlated with the 620 nm PL line intensity. The weak emission lines at 583, 586, and 589 nm are most probable due to $^5D_0 \rightarrow {}^7F_0$ transitions further indicating the existence of different Eu^{3+} centers in GaN:Eu samples grown by IGE technique [6].

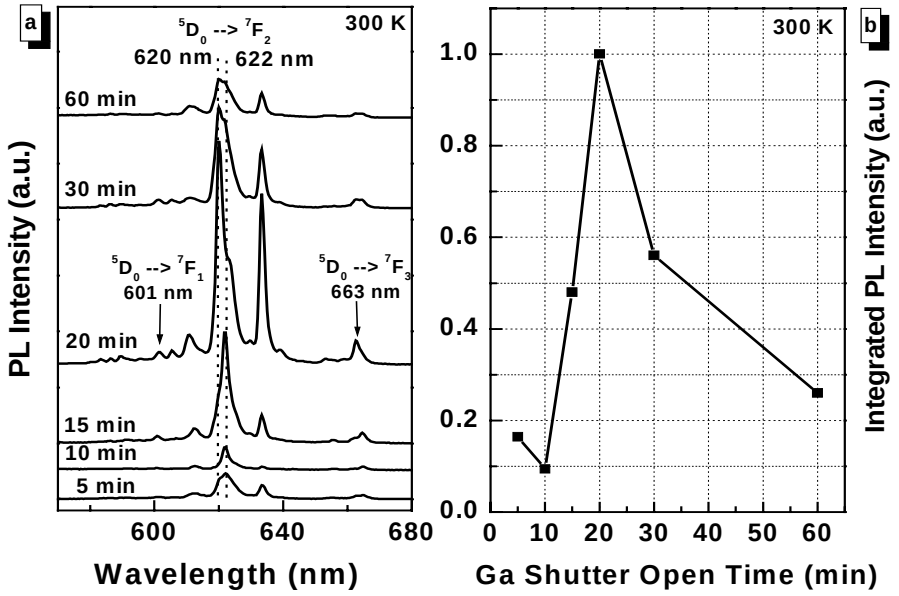

Figure 1. (a) Room temperature PL spectra of GaN:Eu films under above-gap excitation. The group III shutter open times are also indicated in the graph. (b) Integrated PL intensity of GaN:Eu films as a function of Ga/Eu shutter cycling time.

The room temperature PL decay transients under above-gap excitation are shown in Fig. 2. It can be noted that the PL lifetimes varied significantly between the samples. The PL decay transient of the strongest emitting sample (20 min) showed a 1/e lifetime value of only ~54 μs.

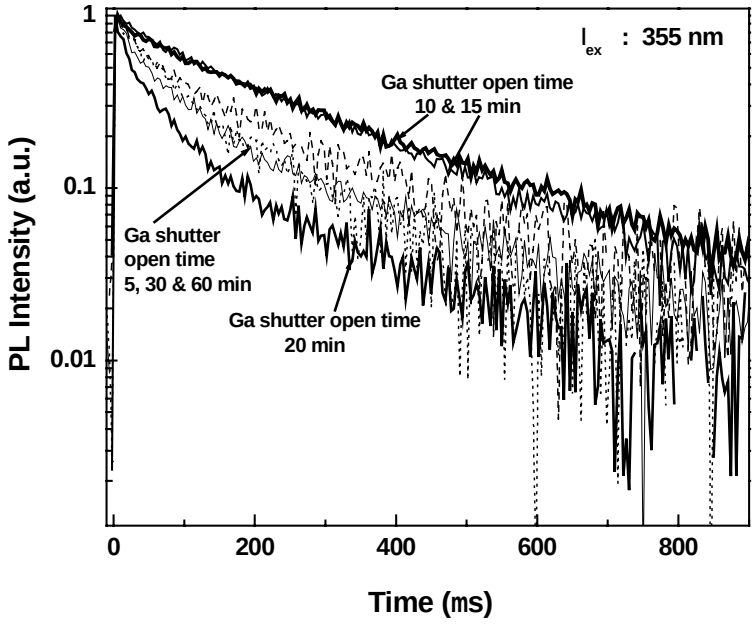

Figure 2. PL decay transients of GaN:Eu films under above-gap excitation (355 nm) at 300 K.

The PL decays of GaN:Eu films with Ga shutter cycling times of 10 and 15 min were nearly exponential with 1/e lifetime values of ~ 208 μs. The 5, 30, and 60 min samples, which have both Eu^{3+} sites, showed PL lifetimes between ~ 75 μs and ~120 μs. The PL decay measurements indicate that Eu^{3+} site 1 (PL peak: ~ 620 nm) has a "short" lifetime of ~ 54 μs and Eu^{3+} site 2 (PL peak: ~ 622 nm) possesses a "long" lifetime of ~ 208 μs.

Figure 3 depicts the temperature dependent PL lifetimes for samples with Ga shutter cycling times of 20 and 10 min. The PL lifetime of the 20 min sample exhibited a large change in lifetime between 15 K and 300 K, as shown in Fig. 3 (a). The 1/e PL lifetime values at 15 K and 300 K were ~ 158 μs and ~ 54 μs, respectively, which shows a ~ 66 % decrease relative to its low temperature value. On the other hand, the PL lifetimes were nearly temperature independent for the GaN:Eu sample with a Ga shutter time of 10 min. For this sample the lifetime decreased by only ~ 17 % relative to its low temperature value [see Fig. 3 (b)]. The large difference in the decay time behavior provides further support for the existence of different Eu^{3+} sites in these samples.

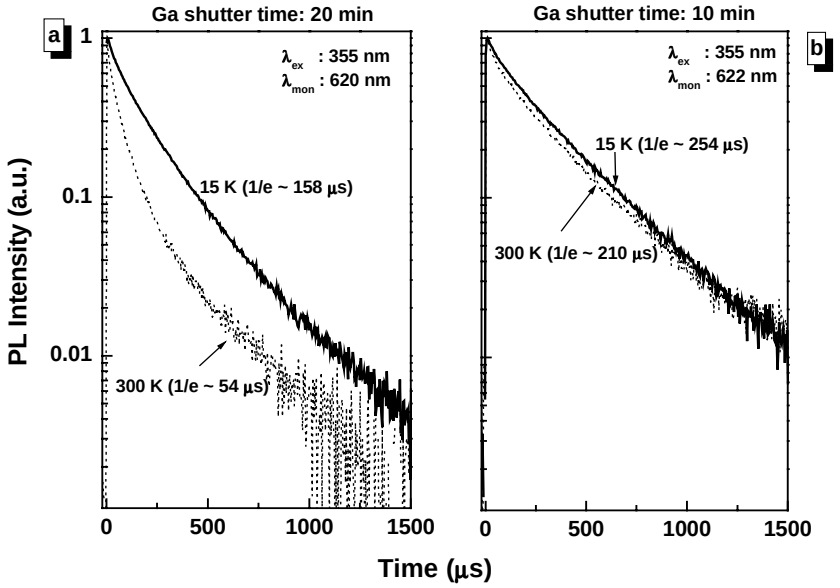

Figure 3. Temperature dependent PL decay transients for the samples with Ga shutter time (a) 20 min and (b) 10 min under above-gap excitation. The 1/e lifetime values are also indicated in the graph.

Below-gap emission Spectra and PL decay

To gain more insight in the Eu^{3+} PL properties of GaN:Eu prepared by IGE, PL spectra were recorded under resonant intra-4f Eu^{3+} excitation using the 471nm output of an OPO system [Fig. 4 (a)]. Nearly identical Eu^{3+} PL spectra with the $^5D_0 \rightarrow {}^7F_2$ emission line at ~ 622 nm were observed for all samples. This observation suggests that Eu^{3+} site 2 is dominant under resonant pumping. The normalized PL spectra under above-gap excitation are shown in Fig. 4 (b) for comparison.

The differences in PL spectra under above-gap and resonant-excitation further indicate that different Eu^{3+} centers were formed in GaN during the IGE growth process. Compared to above- gap excitation, resonant Eu^{3+} excitation preferentially excites only one Eu^{3+} site (site 2).

The PL decay monitored at ~ 622 nm under resonant-excitation showed that the transients are nearly exponential with variations in 1/e lifetimes ranging from ~ 100-215 μs.

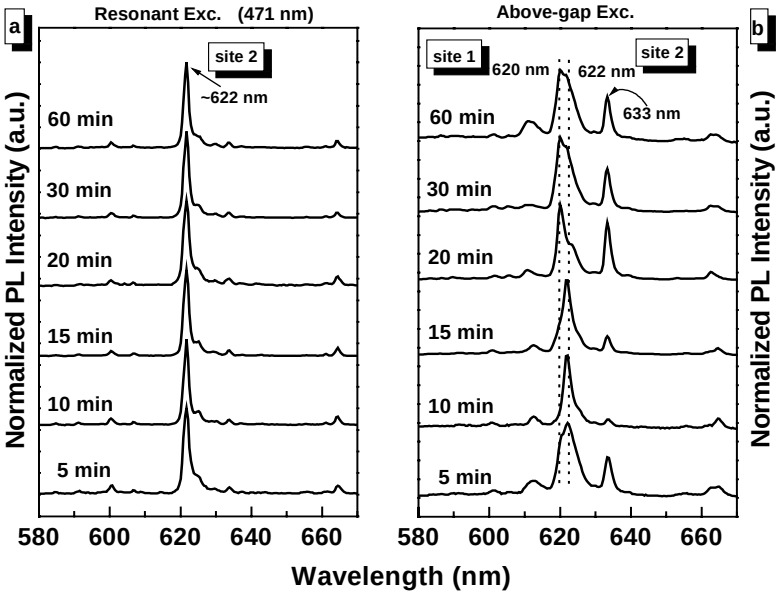

Figure 4. Normalized PL spectra of GaN: Eu under (a) resonant and (b) above-gap excitation. The group III shutter open times during IGE growth are also indicated in the graph.

PL excitation measurements

We recently studied the incorporation of Eu^{3+} ions in GaN: Eu films grown by conventional solid-source MBE (SSMBE) technique and identified at least five Eu^{3+} centers [5]. Initial PL excitation (PLE) studies at room-temperature were performed on GaN: Eu samples grown by IGE technique as shown in Fig. 5.

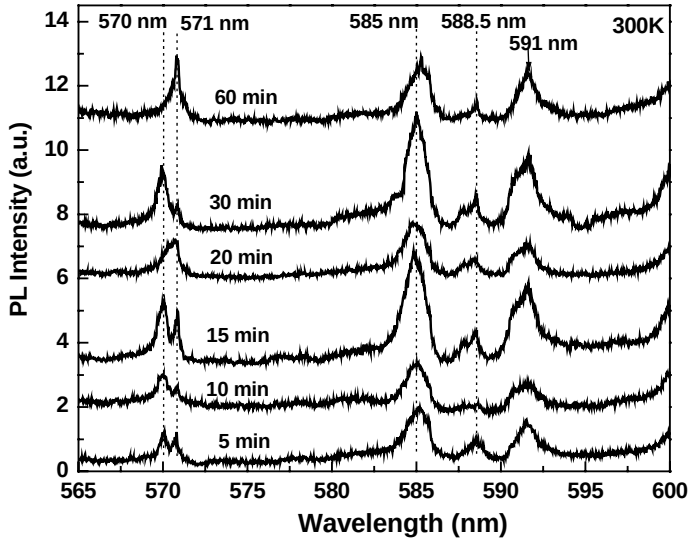

Figure 5. Room temperature PLE spectra of GaN:Eu films with various Ga shutter cycling time.

The Eu^{3+} luminescence was monitored at ~ 622 nm and the excitation wavelength was scanned in the spectral region of the $^7F_0 \rightarrow {}^5D_0$ transition between 565 and 600 nm. Interestingly, the observed PLE spectra were similar to the results obtained from GaN:Eu grown by SSMBE [5]. Three main PLE peaks were observed at ~ 571, 585, and 588.5 nm from all samples. For some samples the ~571 nm lines exhibited a splitting into two lines. The PLE line at 591 nm does not originate from the $^7F_0$ ground state, as previously reported [5]. The obtained PLE spectra further demonstrate the existence of different Eu^{3+} centers in the GaN:Eu samples prepared by IGE growth. An attempt was made to selectively excite the different Eu^{3+} centers using the tunable laser output from an OPO system. However, due to a poor signal to noise ratio, no spectral differences were observed. Further site-selective PL spectroscopy is needed to elucidate the incorporation of different Eu^{3+} sites in GaN sample grown by IGE technique.

SUMMARY

Spectroscopic results on the emission properties were presented on a set of GaN:Eu films grown by interrupted growth epitaxy (IGE). The strongest Eu^{3+} red emission under above-gap excitation was observed for a sample with a 20 min Ga cycling time. Two Eu^{3+} sites with the $^5D_0 \rightarrow {}^7F_2$ PL peaks located at 620 nm (site 1) and 622 nm (site 2) were dominant in the above-gap PL spectra. It was found that Eu^{3+} site 1 exhibited a "short" lifetime (~ 54 μs) and Eu^{3+} site 2 had a "long" lifetime (~ 208 μs). Contrary to above-gap excitation, resonant Eu^{3+} excitation selectively excited only one Eu^{3+} center (site 2). PLE measurement in the $^7F_0 \rightarrow {}^5D_0$ spectral region provided further supported for the different Eu^{3+} centers in these samples. Additional high-resolution PL and site-selective PL studies are required for these samples to obtain a better understanding of the incorporation of Eu^{3+} ions into GaN. Also, efforts to relate the Eu^{3+} PL properties to the crystalline quality of GaN: Eu samples grown by IGE are still in progress.

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